FORMATION AND STABILITY OF WATER-IN-OIL EMULSIONS

by

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ABSTRACT

A review is presented of recent literature, including some Russian literature, concerning the formation and stability of water-in-oil emulsions. An experimental program is briefly described which sought to further elucidate aspects of the nature of the phenomenon of water-in-oil emulsion formation. Possible mechanisms of formation and stabilization are postulated and discussed.

RÉSUMÉ

On présente un survol de publications récentres, y compris en russe, sur la formation et la stabilité des émulsions de type huileux c'est-à-dire eau dans hydrocarbures. On décrit brièvement un programme expérimental destiné à élucider ce phénomène. On propose et discute des mécanismes possibles de formation et de stabilisation.

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1. INTRODUCTION

The tendency for crude oil slicks to form water-in-oil emulsions (mousses) on the sea surface results in substantial changes in behaviour, and effects and necessitates changes in countermeasures approaches. It is obviously desirable to understand, as fully as is possible, the factors which cause an oil to emulsify, and the rate at which emulsification occurs in order that the behaviour of a given oil under given environmental conditions can be assessed. The dominant processes are shown in Figure 1.1. In a previous study Mackay and Zagorski (1982) reviewed the literature to that date on emulsions, devised a rotating flask test for emulsion formation and stability evaluation and hypothesised that stability was controlled by a phase separation phenomenon in which asphaltenes precipitate around (and stabilize) water drops when the oil composition and temperature are appropriate. It was suggested that waxes promote the precipitation of asphaltenes. A tentative mathematical model of emulsion formation was presented.

A careful perusal of the literature has shown that there is a considerable amount of Russian work in this area, little of which has been translated into English, and which has been largely ignored by non-Russians. We have gathered and translated these papers and include a review of that literature.

The methods of analyses for asphaltenes and waxes used in the previous study were judged to be insufficiently accurate, thus some effort was devoted to developing and validating improved analytical schemes. These schemes are described.

Since 1982 there have been other studies and reviews, notably the book by Payne and Phillips (1985) and a number of reports from ongoing studies in

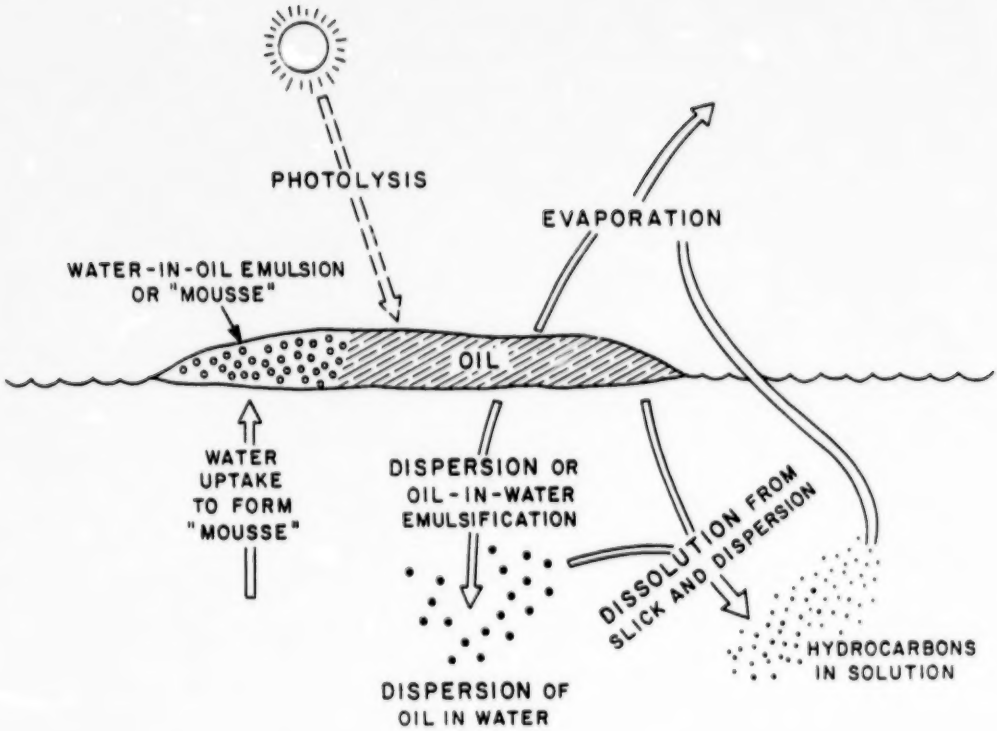

Figure 1.1 Oil Spill Processes

France and Norway. This report is essentially an updated review of that literature, supplemented by descriptions of selected experiments.

An experimental program is described in which the aim was to elucidate the causes of emulsions stability. When testing a variety of "natural" oils it is often difficult to obtain precisely the desired combination of components with which to test a stability hypothesis. An attractive approach is to synthesise oils of the desired content, of for example, asphaltenes. Separating asphaltenes from oil is difficult and many result in chemical change, thus a better approach is to blend natural crude oils to obtain the desired contents. We have been fortunate in obtaining suitable oils, notable Norman Wells Crude Oil which has a very low asphaltene content and Cold Lake crude oil which has a high asphaltene content. These oils were kindly supplied by Drs. Gurak and Cameron of Imperial Oil Ltd., Sarnia.

The findings are discussed and a modified hypothesis postulated which is consistent with the Russian work, our earlier work and with the current results.

Finally, it must be emphasised that the phenomenon of water-in-oil emulsion formation is not yet fully understood, although we believe that we are now closer to a reasonable explanation of the phenomena, which may be sufficient for immediate oil spill analysis and for countermeasures planning.

2. LITERATURE REVIEW

2.1 General

Payne and Phillips (1985) have presented a comprehensive review of the emulsion literature until approximately 1984. This was based on a review for the National Academy of Sciences. Thus a synopsis of their findings can also be found in the NRC report "Oil in the Sea" (NRC, 1985). Subsequent to these reports there has been activity in Norway, as reported in the Proceedings of a symposium on dispersion held in Trondheim in November 1986 (Oceanographic Center-Sintef Group, 1987). In France, there has been a continuing study of emulsion formation and the role of photo-oxidation by authors including Lamathe (1982) and Desmaison et al. (1984).

Another aspect of this issue which has received increasing attention is the use of chemicals to break emulsions or retard their formation. The most recent available report on this subject is by S.L. Ross (1986) in which a surface active chemical was tested which successfully inhibited water-in-oil emulsion formation. Buist and Ross (1987) have also reported on this work.

Canevari (1987) has recently discussed some data on the susceptibility of various crude oils to emulsion formation, an approach which has been well-described for other oil spill processes by CONCAWE (1983).

A recent text edited by Eicke and Parfitt (1987) has a number of interesting papers which are relevant to this issue. Becker (1987) has a chapter on water-in-oil emulsions including reviews of stability, rheology and conductivity. Eicke (1987) describes aqueous nanophases or microemulsions of water in oil, the water particles being colloidal in nature, i.e. 10 to 100 nm in size. Friberg (1987) reviews the stabilization of emulsions by nonionic surfactants and describes the phase behaviour of water-hydrocarbon-surfactant

systems including the formation of liquid crystalline phases. We return to this phase behaviour issue later when discussing the possibility that emulsions are formed as a result of breakdown of these liquid crystal phases.

Table 2.1 (reproduced here from Payne and Phillips, 1985) summarises studies of emulsion formation under laboratory conditions. Only the distillates and very light oils such as Norman Wells, fail to form emulsions. Canevari (1987) has also presented Exxon data showing that most crude oils form emulsions. The emulsions contain up to 80% water, are very viscous and usually light brown in colour.

Payne and Phillips (1985) have also reviewed several case studies in which emulsions were formed. The rate or timing of mousse formation depends on the nature of the oil, level of turbulence and temperature. It appears that oil has two general competitive routes open to it: dispersion into oil in water emulsion, or formation of water in oil emulsion. Light oils generally follow the first (dispersion) route, at least initially. If the oil survives on the sea surface, it may then form a mousse.

The author of this report has attempted to assimilate this considerable body of information and compile a brief statement of our state of knowledge. This is presented in a later section in the discussion.

2.2 Aspects of Hydrocarbon Chemistry

An understanding of emulsion formation can not be obtained unless there is some appreciation of the underlying hydrocarbon chemistry. A convenient review is that of Speight (1981). But it is useful to treat in more detail the probable structures and configurations of the heavier components of oils,

Table 1/ Mousse formation experiments using a variety of fresh and artificially weathered (topped) crude oils in laboratory, outdoor test tank, and field experimental spills.

	Initial Oil Properties									Water-In-Oil Emulsion (Mousse) Properties				
Product Tested	Specific Gravity	Viscosity	Pour Point °C	Wax % Weight	% Asphal-tenes	% Sulfur	V (ppm)	Ni (ppm)	Stable Mousse Formed/ Appearance	Final % Water	Viscosity	Pour Point °C	Bacterial Growth Noted (6 weeks)	References
Libyan (Brega)	0.829	4.13*	7.2	11.4	0.13	0.21	5		Borderline/ dark brown-waxy	78.3			Fairly heavy	Berridge et al., 1968 a,b
Nigerian Light	0.867	5.16*	-15.0	8.5	0.05	0.19	5		Borderline/yellow brown-granular	77.3			Heavy infestation	Berridge et al., 1968 a,b
Iranian Light (Agah Jari)	0.854	5.6*	-20.6	7.0	0.7	1.33	35		Rigid/foamy	79.1			Fairly heavy	Berridge et al., 1968 a,b
Iranian Heavy (Gach Saran)	0.869	8.83*	-12.2	6.7	1.9	1.58	107	37	Rigid/mid-brown	77.3			Very few	Berridge et al., 1968 a,b
Iraq (Kirkuk)	0.845	4.75*	-34.4	6.5	1.3	1.88	25		Rigid/dark brown	78.3			Very few	Berridge et al., 1968 a,b
Kuwait	0.869	9.6*	-31.7	5.5	1.4	2.5	27	9	Rigid/mid-brown	79.1			Some present	Berridge et al., 1868 a,b
Venezuelan (Tia Juana Medium)	0.869	25.0*	-34.4	4.8	3.05	1.54	170	16	Rigid/dark oily brown	73.8			Very few	Berridge et al., 1968 a,b
Bunker C	0.990	2.8×10^7 cP @ 10°C	+7						Rigid and sticky	67	2.9×10^7 cP			Berridge et al., 1968 a,b Twardus, 1980
Light Arabian Crude	0.99	6.04 cS @38 °C									500-800 cS @ 20°C			Solsbury, 1976 Twardus, 1980
Norman Wells	0.83	8.68 cP @10°C	-85						Unstable	50	110 cP @10°C	-48		Twardus, 1980 (additional data original reference).
fn	0.93**		-8**								240**			
Sweet Blend	0.83	14.2 cP @10°C	-35						Unstable	60	450 cP @10°C	-48		Twardus, 1980
	0.94**		-12**								520**			
Sour Blend	0.83		-50											
	0.94**		+18**								3000**			Twardus, 1980
Bow River	0.90		-27											
	0.99**		0**								2150**			Twardus, 1980

Table 3.1 Mousse formation experiments using a variety of fresh and artificially weathered (topped) crude oils in laboratory, outdoor test tank, and field experimental spills. (Continued)

Product Tested	Initial Oil Properties								Water-In-Oil Emulsion (Mousse) Properties					
	Specific Gravity	Viscosity	Pour Point °C	Wax % Weight	% Asphaltenes	% Sulfur	V (ppm)	Ni (ppm)	Stable Mousse Formed/ Appearance	Final % Water	Viscosity	Pour Point °C	Bacterial Growth Noted (6 weeks)	References
Alberta Crude	0.829	8.25 cP @20°C							Stable mousse	70-80% in 30-minute wave tanks	100-200 cP			Mackay et al., 1979
350° Topped Kuwait	0.958	208 cS @50°C	+8		2.0	7% total 3.7	50	15	Stable mousse	50% after 8-10 weeks	2350 cS @50°C	13-15		Davis and Gibbs, 1975
Prudhoe Bay	0.893	19 cS	-10	-	23	-	28.3	13.5	Stable mousse/ light brown	55	2800 cS after 12 days 7800 Cs after 4 months in subarctic wave tank experiments			Payne et al., 1981a; 1983a
									Stable mousse	65	25,000 cS after 11 hrs 30,000 cS after 35 hrs in the presence of ice			Payne et al., 1984b
Gasoline									No emulsion or mousse	Nil				Berridge et al., 1968b
Kerosene									No emulsion or mousse	Nil				Berridge et al., 1968b
Auto Diesel									No emulsion or mousse	Nil				Berridge et al., 1968b
Marine Diesel	0.83	10 cP @10°C	-15						No emulsion or mousse	Nil		17**		Twardus 1980; Berridge et al., 1968b
	9.87**		-8**											
Lube Oil 600									Unstable emulsion					Berridge et al., 1968b
Lube Oil 2500									Fluid emulsion but no mousse					
Heavy naph Lube									Fluid emulsion but no mousse					

* Kinematic viscosity (cS) at 100°F
** Specific gravity and pour point after 4 weeks pan evaporation under atmospheric conditions (no water added except for occasional precipitation).
*** 93% of water shed after standing 15 minutes
**** 88% of water shed after standing 15 minutes

Table 2.-1 Mousse formation experiments using a variety of fresh and artificially weathered (topped) crude oils in laboratory, outdoor test tank, and field experimental spills. (Continued)

Product Tested	Initial Oil Properties								Water-in-Oil Emulsion (Mousse) Properties				
	Specific Gravity	Viscosity	Pour Point °C	Wax % Weight	% Asphaltenes	% Sulfur	V (ppm)	Ni (ppm)	Stable Mousse Formed/ Appearance	Final % Water	Viscosity	Pour Point °C	Bacterial Growth Noted (6 weeks)	References
Lloydminster	0.90	86.8 cP @10°C	-52						Stable	60	2800 cP @10°C			Twardus, 1980
	0.98**		-9**								2579**			
Weyburn Middle	0.89	29 cP @10°C	-28						Stable	60	4150 cP @10°C	-2.5		Twardus, 1980
	0.99**		-3**								1250**			Twardus, 1980
				Added % wax & % asphaltenes										
Topped 200+ Kuwait (dewaxed & deasphaltenized)				0 0					Unstable emulsions***					Bridle et al. 1980 a,b
				5 0										
				0 1.4					Unstable emulsion****					
				5 1.4					Stable mousse					
				5 0.14					Stable mousse					
Lube Oil									No emulsion	<1				Bridle et al., 1980 a,b
Lube Oil + 5% asphaltenes/wax mix									Stable emulsion	54	0.01-0.03 um water droplet size			Bridle et al., 1980 a,b
Lube Oil +10% asphaltenes/wax mix									Stable emulsion	67	0.01 um water droplet size			Bridle et al., 1980 a,b
Venezuelan (Quiripa)	0.859			-	5.2	1.66	105	18	Mousse and tarballs and flakes formed after few days in wave tank at 20°C (85% water-in-oil in first few days; dropped to 75% over 4 months). Specific gravity approached 1.0.					MacGregor and McLean, 1977
Libyan (Sarir)	0.843			20	0.15	0.14	0.5	5						MacGregor and McLean, 1977
Algerian (Zarzaitine)	0.818			5.3	0.08	0.09	1	1	Unstable emulsion					MacGregor and McLean, 1977
Nigerian Medium	0.892			4.6	0.1	0.25	0.8	7						MacGregor and McLean, 1977

especially the asphaltenes, since they clearly play a key role in stabilizing emulsions.

In studies of the heavier components of oils, four groups may be identified: Saturates, Aromatics, Resins (or polars or polar aromatics) and Asphaltenes. The waxes are part of the saturates.

Saturates

The saturates are believed to consist of normal and branched alkanes and cyclic structures containing 1 to 5 rings and various degrees of alkylation. The cyclic structures dominate in the more degraded oils. Some of the typical cyclic structures are shown in Figure 2.1 (Mazza, 1987).

Aromatics

This fraction is fairly similar to the cyclic alkanes in structure but contains aromatic rings. Low concentrations of oxygen and nitrogen are found. Some sulfur is present in thiophene rings and as sulphide. Figure 2.2 illustrates a typical series (Mazza, 1987). Also present are polycyclic aromatic hydrocarbons and alkylated derivatives.

Resins

This fraction contains oxygen, nitrogen and sulfur compounds and is more polar in nature. They contain, as shown in Figure 2.3 (Mazza, 1987), carbazoles, fluorenols, fluorenones, carboxylic acids and sulfoxides. These substances are likely to be attracted to water interfaces and may participate in exchange with electrolytes in water solution.

Asphaltenes

This is the most complex group and is believed to consist of condensed polycyclic aromatic material with alkyl substitution. There may be 6 to 20 rings, some parent hydrocarbons being shown in Figure 2.4 (Mazza, 1987).

Molecular weights thus may range from about 500 to 10,000, with a median of perhaps 2,000. Some nitrogen and sulfur may be incorporated in the rings. There is an opinion that the saturates are primarily of plant origin (and show the characteristic terpene structure) and by a gradual process of aromatization these are converted to aromatics or resins, which subsequently polymerize to asphaltenes.

The asphaltene molecules apparently associate in solution to variable extents, probably by forming multi-layered aromatic sheets are shown in Figure 2.5 (Mazza, 1987). The sheets are held together by van der Waals attractions and π bonding. Typical sheet to sheet dimensions are 0.36 to 0.38 nm, thus a 5 sheet asphaltene "micelle" may be of dimensions 1.8 nm. Spacing between graphite sheets in 0.34 nm, thus essentially the same type of packing may occur, but less "perfect" in the case of asphaltenes because of sheet to sheet differences and the presence of alkyl groups.

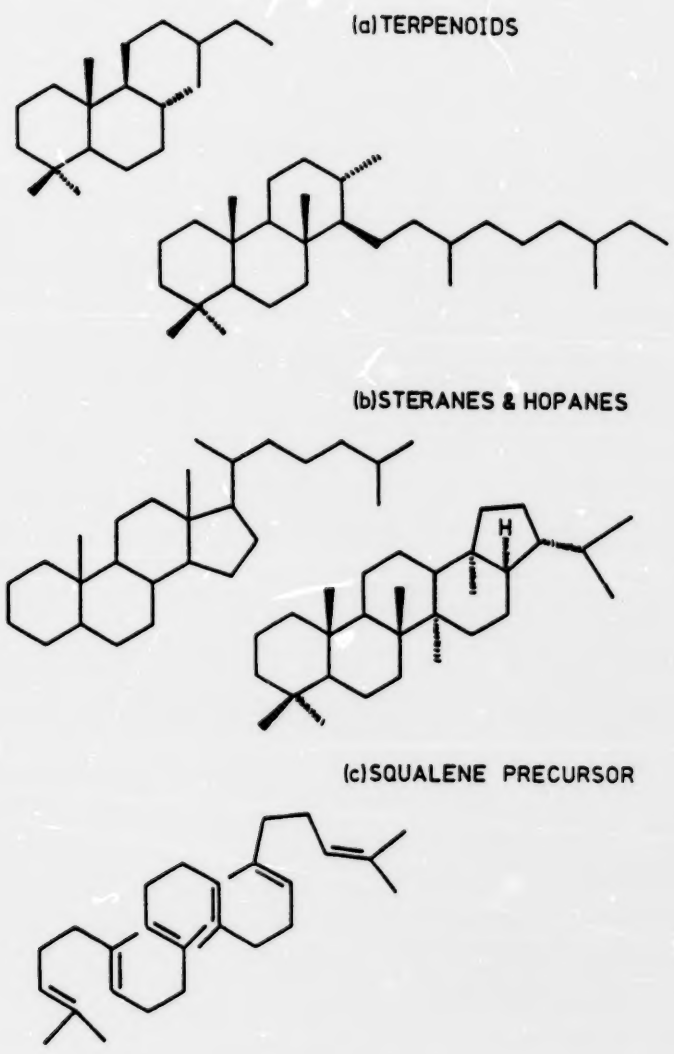

Figure 2.1 Important chemical structures in the saturate fraction.

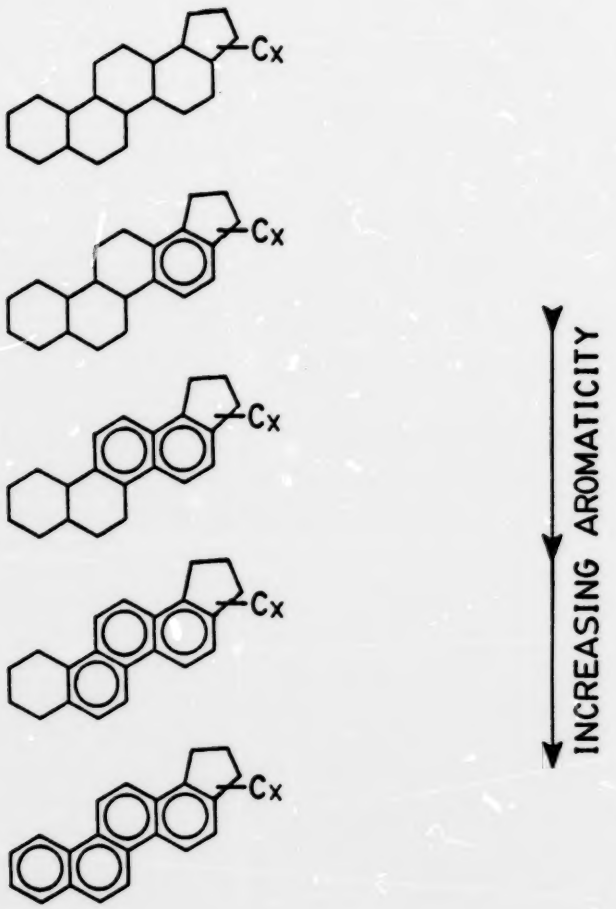

Figure 2.2 Increasing aromaticity within a homologous series of compounds in the aromatic fraction.

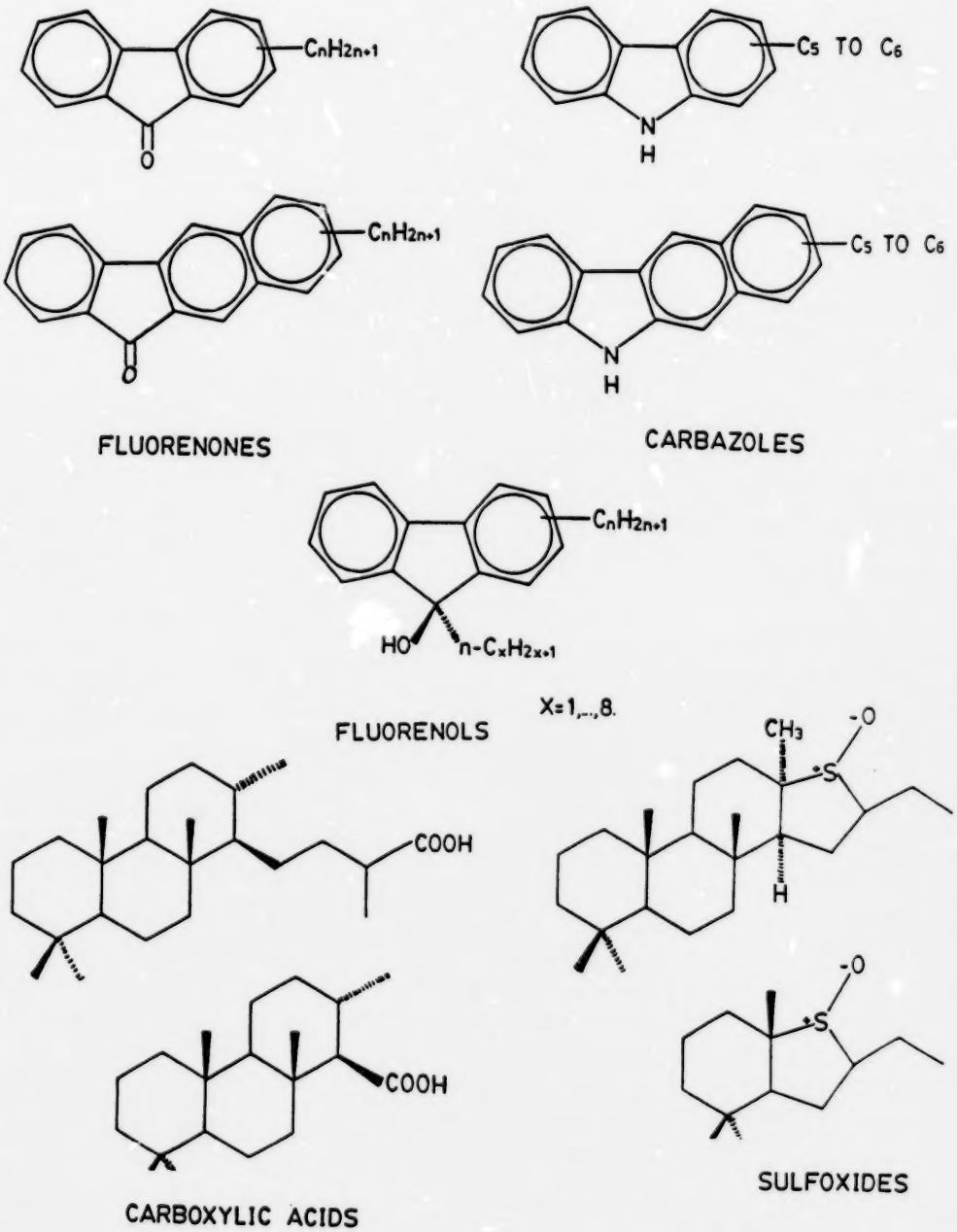

Figure 2.3 Components of Resin Fraction

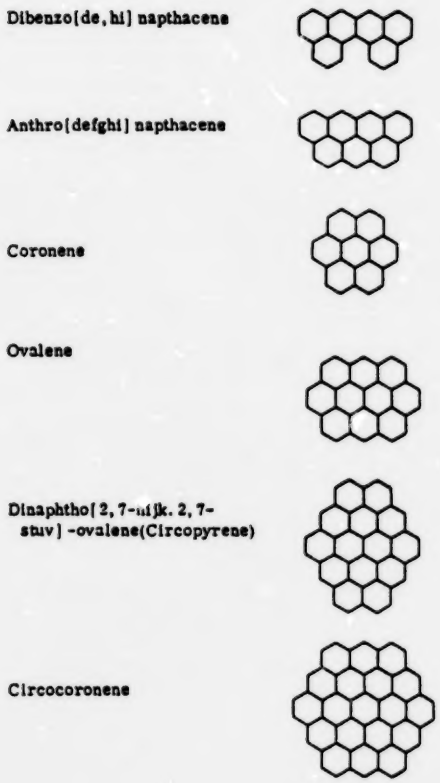

Figure 2.4 Condensed aromatic nucleii believed present in the resin and asphaltene fractions.

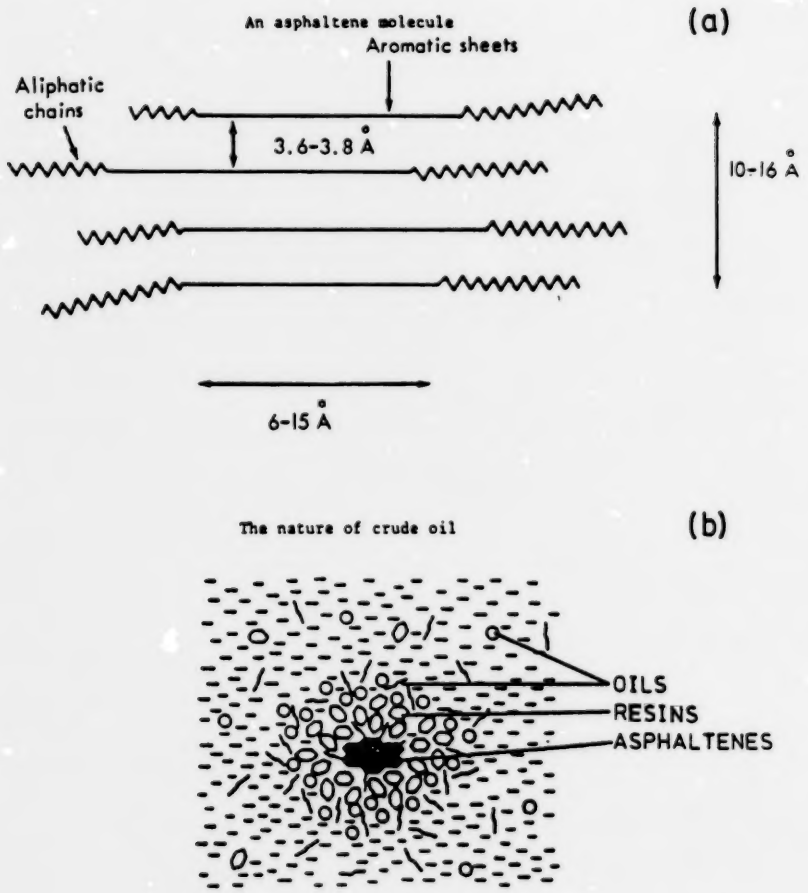

Figure 2.5 The physical nature of an asphaltene micelle in Petroleum.

2.3 Review of Russian Literature

Some 28 papers published in Russian Journals, mostly in Russian, were obtained and translated.

They are separately referenced at the end of this report. The following is a brief general account of the findings of this series of papers.

Asphaltenes

A variety of analytical methods has been used to study asphaltenes including IR spectroscopy, NMR, X-ray and elemental analyses. They are regarded as condensed polycyclic aromatic compounds containing heteroatoms, notably S, N and O with side aliphatic chains. Their molecular weight varies from 780 to 1300 (5) or 886 to 3300 (4); the results depend on the crude oil source. This implies a structure containing possibly 70 carbon atoms or some ten aromatic rings with various extents of fusion and with abundant side chains. Because of the variability in molecular weight, concentrations are expressed in mass rather than molar quantities.

The asphaltenes are believed to agglomerate or form "micelles" or what is here loosely termed "particles". This agglomeration is enhanced by Van der Waals forces between flat aromatic rings and hydrogen bonding between polar groups. The phenomenon is not attributed to surface activity (3). The "tars", also form particles but with fewer units (2,3,4,6,7,8,9,10) which contain more alkane character. The molecular weight of the particles has been estimated by turbidity and refractive index methods. The properties of artificial crude oils of benzene, heptane and asphaltenes have been studied. At low asphaltene content as the oil becomes more aromatic (i.e., as benzene concentration is increased from 0 to 10%) the particle stability increases but it then falls off at higher benzene concentrations. Generally the asphaltenes

are in the form of particles with a molecular weight ranging from a few thousand to a hundred thousand or more. Assuming a density of 1000 kg/m^3, cubic particles of the following molecular weights would have the following approximate dimensions.

Side = 10^4 $(M/N)^{0.33}$ μm M = mol wt (g/mol) N = 6 x 10^{23} (Avogadro's No.)

M	side (μm)	(nm)
10^3	.0012	1.2
10^4	.0026	2.6
10^5	.0056	5.6
10^6	.012	12
10^7	.026	26

These particles which are large from a molecular viewpoint are thus still very much smaller than a small (1 μm) water emulsion particle in oil. A typical molecular weight may be 10^4 corresponding to particles in the 2 to 4 nm size range. Typically, the particles have dimensions of 1/100 to 1/1000th of the water droplet.

Asphaltenes are insoluble in pure alkanes such as n-heptane thus the usual analytical procedure is to dilute 1 volume of oil with 40 volumes of n-heptane or iso-octane, allow precipitation to occur, then filter off the asphaltenes. Apparently under these conditions there is appreciable or total aggregation. Only in very dilute solution in aromatic solvents are the asphaltenes in mono-molecular form.

There have been investigations of stability to sedimentation of asphaltenes (23); as expected, the smaller the particles, the slower is the sedimentation rate under centrifuging conditions. The most stable solutions occur when the number of cyclic rings is large and the alkene side chains fewer or shorter. Addition of aromatic solvents stabilized (i.e. gave a smaller particle size) to the asphaltenes.

Emulsion Stability (4,10,12,13,14,15)

Various methods of measuring emulsion stability have been proposed. The ratio of water volume before and after centrifuging under defined conditions (e.g. 3000 rpm, 5 minutes, 20°C) has been used, as has the concentration gradient formed on centrifuging. A method has been used in which the emulsion is dissolved in a 1:3 toluene:heptane mixture and centrifuged for 10 min at 4000 rpm and 20°C to give upper and lower layers. The respective asphaltene contents of the layers are determined by evaporation.

Since the primary interest is the de-emulsification of produced crude oils, the most common method of quantifying emulsion stability is to measure the amount of de-emulsifier needed to break the emulsion. The de-emulsifier (e.g. DISOLVAN 4411) is added at a dosage of typically 50 g/tonne of oil. A stable emulsion (e.g. 10 to 16% asphaltene content oil) may break to the extent of 10 to 50% water loss under these conditions. Generally the factors increasing emulsion stability are high asphaltene content, high density, high viscosity, and distilled rather than saline water.

It is believed that the asphaltene particles gather at the oil-water interface and form a mechanical skin loosely termed here a "barrier" which prevents coalescence (19). This is similar to the emulsion stabilizing effect of mineral and coal particles (2). The layer may also contain alkanes or

waxes, tar particles and other polar compounds. It is possible that polar surface active compounds accumulate at the water-oil interface between the asphaltene or wax particles and the water. There is evidence that these polar surface active components play a key role because they reduce emulsion stability.

Microcrystals of waxes are also believed to stabilize emulsions but because of their hydrophobic nature they require the presence of surface active polar substances to facilitate their location at the oil-water interface. These wax-stabilized emulsions require the use of different de-emulsifiers from the asphaltene-stabilized emulsions. It is thus possible that surface active compounds (present naturally or produced photolytically) stabilize wax emulsions but they are not needed for stabilization of asphaltene emulsions.

The long term stability of emulsions is strongly influenced by their anti-oxidative character (17). Natural and introduced oxidation inhibitors presumably prevent or reduce the formation of polar groups and prevent the subsequent increase in concentration of surface active material which may migrate to the oil-water interface and there stabilize the emulsion. Asphaltene-stabilized emulsions are less sensitive to alteration by this process than wax-stabilized emulsions.

Ingenious experiments have been done in which an oil film is compressed between two water layers and the force necessary to deform the film is measured (2). As the oil film thins the force starts to increase at approximately 200 μm and reaches a maximum at 80 to 100 μm, then it declines rapidly. This effect is attributed to a mechanical barrier at the oil-water interface which is stable and resists deformation at a thickness of down to

100 μm, then it tends to fail as the barrier is broken and water-water attractive forces come into play. Addition of de-emulsifier reduces the deforming force necessary. Increase in temperature results in a smaller maximum force at greater distance possibly because the particles are less orderly.

Emulsion Stability Number (4,18)

It has been proposed that a dimensionless number N_S be used to characterize emulsion stability when asphaltenes act as the stabilizing agent

$$N_S = AP/SB$$

where A is asphaltene content (mass ratio)

P is paraffinic content (ratio of mass alkane C to total oil mass)

S is silica gel resin content

B is aromatic content (ratio of mass aromatic C to total oil mass)

The ratio P/B is thus the ratio of alkane to aromatic carbon. These concentrations are determined by standard methods. The silica gel resins are believed to have a smaller molecular weight than asphaltenes and have long alkane side chains (Speight, 1980). They may co-precipitate with asphaltenes, but by doing so they reduce the size or stability of the particles and act essentially as a deflocculant.

As N_S increases from 0 to 0.5 the strength of the interfacial oil films described earlier greatly increases then it levels off at N_S exceeding 0.5 when there is presumably a stable mechanical barrier. The dosage of de-emulsifier is also dependent on N_S, being very low if N_S is less than 0.5 but increasing markedly as N_S reaches 0.5 and greater. This relationship is used to determine the required dosage of emulsifier.

The mechanism of de-emulsification is believed to be such that the agent is surface active with a tendency to gather at hydrophilic sites and render them hydrophobic. This reduces the tendency for the particle to accumulate at the water interface and to agglomerate to form larger particles by polar interactions. Essentially, the de-emulsifier tends to drive the stabilizing particles from the water interface into the bulk of the oil. A considerable amount of work has been done on the relationship between the amount of de-emulsifier required and the amount of natural or photolytically induced surface active material present. Apparently, the de-emulsifier is able to displace the naturally occurring stabilizers which are present at area concentrations of 16 to 200 x 10^{-8} g/cm^2. Greater amounts of de-emulsifier are required if there are naturally occurring stabilizers present.

One tonne of emulsion of close-packed 10 μm water spheres will contain typically 0.7 m^3 of water with an area to volume ratio ($\pi d^2/\pi d^3/6$) or 6/d m^2/m^3 or 0.7 x $6/10^{-5}$ or 4.2 x 10^5 m^2 or 4.2 x 10^9 cm^2. To cover this surface to a depth of 1 nm requires 4.2 x 10^{-4} m^3 or 420 g approximately. Usual dosages are approximately 100 g/tonne but possibly as high as 1000 g/tonne. If the emulsion is asphaltene-stabilized a lower dosage is usually needed, possibly because it has less natural stabilizing material present. The wax stabilized emulsions by their nature must have appreciable concentrations of stabilizers thus their displacement requires more de-emulsifier.

3. EXPERIMENTAL

3.1 Analytical Methods

In previous studies the methods of quantifying asphaltenes and other groups were judged to be insufficiently accurate for the purpose of elucidating the mechanism of emulsion formation stabilization, hence some effort was devoted to improving these methods. The experimental work is not described here in detail, only the final recommended procedure being presented.

Asphaltenes

Asphaltenes are the solubility class that is precipitated from crude oils by the addition of a minimum of 40 volumes of n-heptane at room temperature (Bunger and Li, 1981).

Equipment, Reagents, Materials

i) technical centrifuge I.E.C. model K or equivalent

ii) standard centrifuge bottles

iii) 3 aluminum foil bowls of different size

iv) vacuum drying apparatus

v) solvents: dichloromethane, pure grade
n-heptane, pure grade

vi) analytical balance

About 3 g of crude oil is accurately weighed and dissolved in 150 mL of n-heptane. The solution is rotated for 10 minutes at 2000 rpm in the centrifuge at a centrifugal force of 100 g. The liquid over the precipitate is removed by careful decantation. About 20 mL of fresh n-heptane is added, shaking the bottle energetically to prevent the precipitate from sticking to the walls of the bottle. The suspension is rotated for 5 minutes at 2000 rpm

and the liquid over the precipitate again removed by careful decantation. 20 mL of dichloromethane are then added to dissolve the precipitate. Three aluminum foil bowls of different size are weighed and the solution transferred to the smallest bowl. The bottle is rinsed with dichloromethane and the washings transferred to the smallest bowl. This bowl is placed in the biggest bowl and covered with the medium one upside down. The contents are evaporated under vacuum at room temperature for 12 hours and the three bowls weighed. The weight fraction of precipitated asphaltenes can then be determined.

Saturates and Aromatics Contents

The separation of a mineral oil by silica gel chromatography into saturated and aromatic fractions has been used extensively since 1958 (Hodges, 1974). However, all those methods refer to the petroleum products with a boiling point of at least 200°C. The serious disadvantage is that the partly weathered crude oil still contains some hydrocarbons of lower boiling point. Only for particularly heavy crude oils such as Cold Lake crude oil is this fraction insignificant and can be neglected.

Those heavy oils may be susceptible to emulsion formation. Standard methods for separation of representative aromatics and non-aromatic fractions of high boiling oils by elution chromatography - ASTM D2549-76 was adopted.

Alternatives are: ASTM D936-55(1973)

ASTM D1019-68(1973)

or the modification recommended by Hodges (1974) can be used.

Waxes

The term " paraffin wax" is restricted to the colorless, translucent, highly crystalline material obtained from the light lubricating fractions of paraffinic crude oils (wax distillates). The commercial products that melt in

the approximate range of 50 to 65°C contain mostly n-paraffins with some isoparaffins. Dewaxing of heavier fractions leads to semi-solid materials known as petrolatums. Solvent de-oiling of the petrolatum or of heavy, waxy residual results in dark colored waxes of sticky, plastic-to-hard nature. Although amorphous in appearance, these waxes are actually composed of exceedingly fine crystals and contain, in addition to n-paraffins, appreciable amounts of isoparaffins and long-chain cyclics (Speight, 1980).

After removal of asphaltenes the excess of n-heptane is evaporated. A volume of acetone: benzene (2:1 volume ratio) mixture ten times the oil volume is added. The liquid is chilled to 0°C for 2 hours and is then filtered while cold. The precipitate is the waxes.

An alternative method employs 5:1 methylethylketone to oil volume ratio requires chilling to -10°C. This method is recommended for oils of low viscosity and low asphaltene content.

3.2 Emulsion Formation Tests

In the first series of test the rotating bottle apparatus devised by Zagorski (1982) was used with a water to oil volumetric ratio of 3:1 and various synthetic oils containing added waxes and asphaltenes. It was found that this ratio was not optimal and in a second series the emulsification system was improved by increasing the water to oil volume ratio to 9:1 by decreasing the volume of oil. Oil mixtures were prepared by blending Norman Wells and Cold Lake crude oils.

In the first series of experiments, 2 litres of Norman Wells crude oil were dewaxed at a low temperature (-40°C) using the minimum of methylethylketone (1:1 volume ratio). The methylethylketone and the dewaxed

Norman Wells crude oil were separated by rectification using a twenty-theoretical-plate Hemple rectification column. The entire wax content was recovered as determined by an independent analysis using a 5:1 volume ratio and a temperature of -10°C.

The dewaxed oil was divided into 25 mL portions. Asphaltenes extracted from La Rosa crude oil, (using the standard precipitation method as described earlier) were introduced into each sample. Good mixing was assured by heating the oil to the boiling point in a distillation apparatus adjusted to full reflux. A few droplets of benzene had to be added to ensure quantitative transfer of asphaltene from aluminum bowls to the oil.

Refined wax, supplied by Imperial Oil Ltd., was added to each sample. Melted wax (80°C) was poured into the boiling oil. The mixture was then boiled in a distillation apparatus for at least one hour. After the homogeneity of the oil-asphaltene-wax mixture was assured, 25 mL of this mixture was transferred to a centrifuge bottle and 75 mL of salt water was added. The mixture of salt water and synthetic crude oil was rotated in the rotary shaker.

The fraction of oil remaining in the emulsified form (F) was reported as a function of asphaltene and wax content. Speed of rotation, time of rotation, time of settling and the diameter of the settling vessel were varied. The emulsions were divided into three groups on the basis of the oil volume fraction emulsion value as shown in the figures. The values of F were determined with an accuracy of approximately 5%.

A 1:3 synthetic oil - salt water volume ratio was used in all experiments. Experiments were conducted at room temperature of 21°C. Both asphaltene and wax contents refer to the parent synthetic oil.

Figures 3.1 and 3.2 give typical results at rotation speeds of 21 and 65 RPM using the 56 mm diameter bottle rotated for 12 hours then settled for 12 hours. The lower left region in both figures corresponds to a region in which there is negligible emulsion formation. The line separating this region has an equation of approximately (in percentage terms)

$$W + 2.5\ A = 5$$

implying that if the sum of the wax content (W) and 2.5 times the asphaltene content (A) is less than 5, then emulsions do not form. Asphaltenes appear to be 2.5 times more effective than waxes. The region is a little smaller with more turbulence.

The very stable emulsions (shown as squares) occur at 65 RPM when approximately

$$W + 5\ A > 15$$

i.e. asphaltenes are five times more effective.

At 21 RPM there appeared to be insufficient turbulence to induce emulsion formation. The high viscosity oils (e.g. wax greater than 12%) would not form emulsions. It is believed that if they could form emulsions, they would be stable.

Similar results were obtained in other tests, varying parameters such as settling time, vessel diameter and rotation speed.

It was concluded that a better experimental system would be to reduce the oil volume to give a 1:9 oil to water ratio since this would avoid "starving" the oil of water.

A series of tests was conducted under these conditions and gave similar results. It was concluded that this ratio gives more reasonable results.

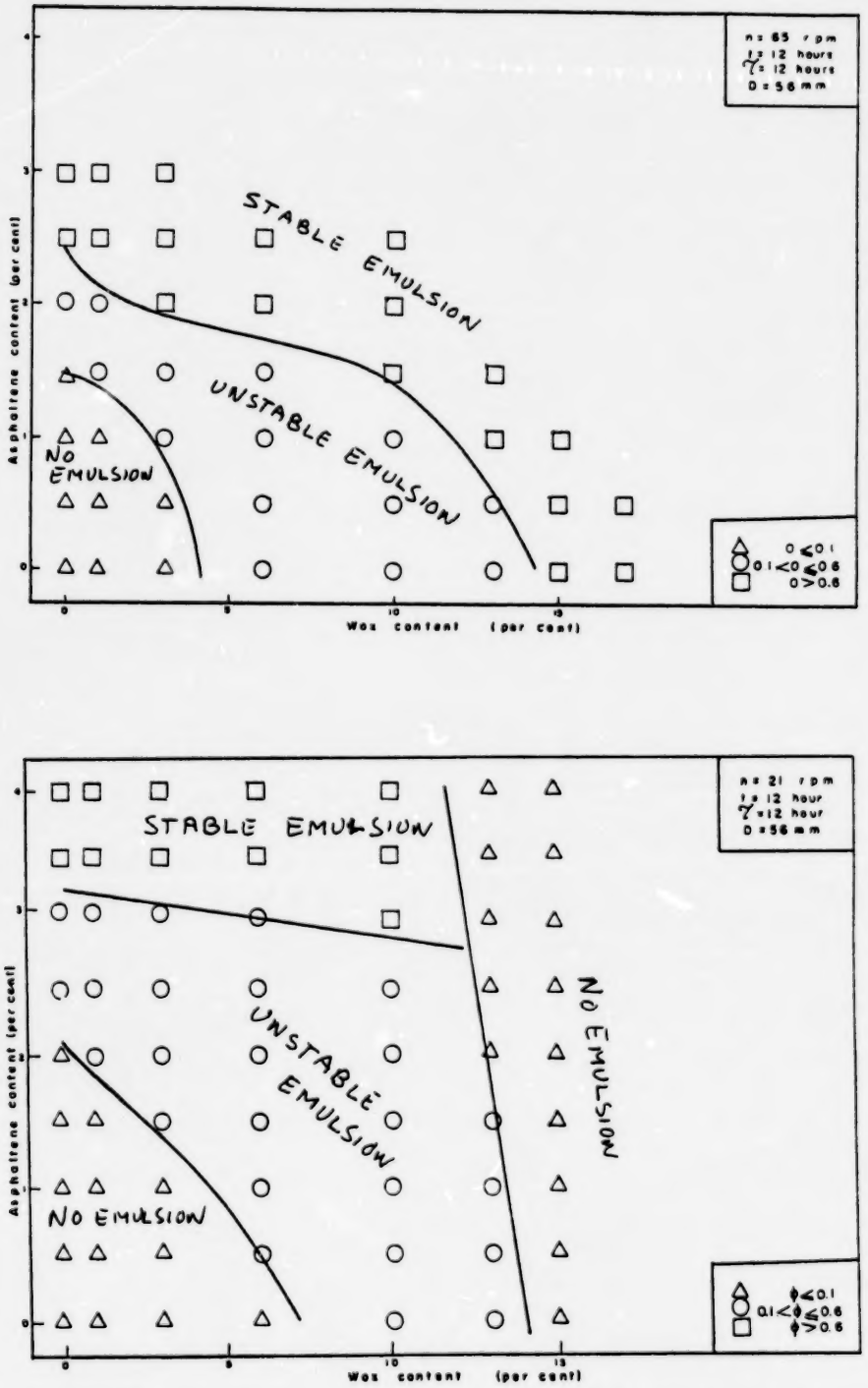

Figure 3.1 and 3.2. Plots of extents of emulsion formation at high turbulence (65 RPM) above, and low turbulence (21) RPM) below. The high wax content oils in the lower diagram were too viscous to form emulsions at the prevailing level of turbulence.

3.3 Resistivity Measurements

A series of experiments was conducted to explore if the presence of a mechanical barrier to coalescence could be detected by measurement of resistivity.

The electrical resistivity measurements were done using a Hewlett Packard High Resistivity Meter 4329A for viscous emulsions and a glass cylindrical cell for the measurement of fluid resistivities. Resistance values in the high megaohm and teraohm regions were subject to wide variation in measured values depended on applied voltage. To make the resistivity measurements comparable, the measurements were done using the same voltage. The measurements were repeated at least five times for the purpose of statistical evaluation of their quality. Relative standard deviation, defined as a ratio of standard deviation to the mean measured value, was measured.

Both the stable and unstable water-in-oil emulsions may be considered as systems consisting of three types of resistive media.

First are solid particles of molecular dimensions, predominantly waxes and asphaltenes. The electrical resistivity of waxes was confirmed to exceed the upper limit of resistivity measurements of the High Resistance Meter of 10^{15} ohm cm. Second, crude oils have an electrical resistivity which varies depending upon their chemical content, in particular, polar hydrocarbons, aromatics and alkanes. Generally, it remains within the range of resistivity measurements of the High Resistance Meter namely 10^{6} to 10^{15} ohm cm. The electrical resistivities of some pure hydrocarbons were also measured at room temperature. Third, salt water has an electrical resistivity which decreases with increasing concentration of salt, but even the resistivity of tap water was below the lower limit of the resistivity measurements of the high

resistance meter, i.e. below 10^6 ohm cm. The electrical volume resistivities of the forming water-in-oil emulsions and those of their respective parent crude oils were measured.

There are two extreme "models" of resistance as a function of emulsion behaviour. If there is no barrier or heterogeneity in the continuous (oil) phase the emulsion will tend to have a resistance similar to that of sea water raised somewhat by the necessity of the current having to flow through films of oil between droplets. If the volume fraction of oil is F_o and the resistivities are V_o for oil and V_w for water then for a path L and area A, the resistance R for mixtures should be approximately

$$R = (F_o V_o + (1-F_o)V_o)\ L/A$$

i.e., it will vary from V_w L/A to V_o L/A.

If this is not observed it may indicate that there is a barrier between oil and water. In an extreme case, if the water is surrounded by a totally insulating barrier the resistance will be given by

$$R = V_o\ L/A_o$$

where A_o is the cross sectional area of the oil and will be approximately $F_o A$. R will thus increase above the value of the parent oil by a factor $1/F_o$ or typically 4. Measurement of emulsion resistance is thus a sensitive test of the presence of insulating material around the highly conductive water.

Table 3.1 gives the resistivity (ohm cm) of several hydrocarbons and crude oils at 20°C at 100 volts.

TABLE 3.1

Resistivities of Hydrocarbons and Crude Oils

Substance	Resistivity
benzene	1.1×10^{11}
n heptane	1.3×10^{12}
toluene	3.2×10^{11}
Arabian light	1.5×10^{9}
Weathered Arabian light	1.4×10^{11}
Arabian heavy	1.8×10^{9}
Cold lake	3.0×10^{11}
Norman Wells	2.0×10^{9}

The resistivities of Norman Wells - Cold Lake oil mixtures were also measured.

It was found that as the oil-water mixture was rotated the resistivity of the oil started at below 10^6 ohm cm then rapidly increased to approximately 10^9 ohm cm which coincided with the formation of a stable emulsion which was brighter in colour. The emulsion resistivities were usually a factor of 2 to 5 greater than those of the parent oil confirming the presence of a highly resistant barrier which is presumably asphaltenic or wax. The rapid increase in resistance apparently corresponds to the closure of the last gaps in the barrier around the water droplets.

It is concluded that measurement of resistivity may be a convenient method of testing for the presence of a "barrier", since it is apparent that the barrier effectively insulates the water drops.

4. DISCUSSION

From the Russian work, these and other studies but notably the work of Desmaison et al. (1984), it is possible to postulate a more reliable mechanism for emulsion formation and stabilization.

The oil phase consists of a hydrocarbon medium containing a suspension of particles of asphaltenes and waxes and possibly mineral matter. The extent of aggregation into particles depends on the concentration of the asphaltenes and the waxes and the aromatic-alkane character of the medium. More aromatic oils tend to be more effective solvents for asphaltenes and particle aggregation is reduced, i.e. there are more, smaller particles. The degree of aggregation of asphaltenes is also influenced by the presence of resins which act to inhibit formation of large particles. The wax crystals may adsorb some surface active material.

The formation of the emulsion involves the creation of a considerable area of oil-water interface with a corresponding energy requirement. Apparently there is normally insufficient energy available until the oil-water interfacial tension falls to a few mN/m. The presence of electrolyte is critical in this process since if fresh water is used the interfacial tension falls much less. It thus appears that carboxylic or phenolic acid groups in the oil may play an important role as surface active agents, their behaviour being modified by combination with cations. As Desmaison et al. (1984) have shown, acidification increases interfacial tension thus it may be the sodium (or other) salts which are the key agents.

Formation is enhanced by turbulence, but it may be retarded by high oil viscosity, since the oil resists distortion.

A recurring problem is how the water drop enters the oil. It seems unlikely that a volume of water of size 1 μm simply becomes engulfed by the oil, because this would result in appreciable distortion of the oil-water interface. It is possible that when two oil drops coalesce a small amount of water becomes trapped between the oil masses and forms small water drops. The larger water drops settle out leaving behind a population of small drops.

Another possibility is that the presence of oxygenated species increases the solubility of water in the oil, especially near the interface where they tend to accumulate. Periodically, as a result of turbulence, this water-rich oil is mixed into the bulk of the oil. But the oxygenated species migrate back to the water interface leaving the water in a supersaturated condition in the oil. The water then precipitates out as small droplets. This speculative mechanism is attractive because it provides a method for water drops to be created in an oil without a water particle actually having to penetrate the oil-water interface. An argument in support of this hypothesis is that if a stable emulsion starts to form as a result of an interfacial barrier or film of high interfacial viscosity, surely this barrier will impede the migration of water into the oil as well as impeding coalescence.

If this mechanism is correct, the reduction in interfacial tension is not itself the important process - it is merely a factor which occurs simultaneously with the formation of oxygenated species which help to dissolve water in the oil.

There is a considerable literature on liquid crystalline phases of oil, surfactant and water which behave approximately as has been described above. These are ordered liquids which have certain regimes of stability. The paper by Friberg 1987 gives examples.

It is emphasized that this is a hypothesis which may be in error. Clearly a mechanism does exist and it coincides with establishment of a low interfacial tension.

When a water particle enters or forms in the oil it tends to accumulate around its interface any available polar surface active material and particles of asphaltene and wax. The presence of a two dimensional area favours the formation of a skin or layer of these particles. Asphaltene particles thus tend to form a surface layer or barrier which is essentially solid and has the strength necessary to resist deformation as may occur when two water drops collide and tend (unsuccessfully) to coalesce. It also has a very high electrical resistivity (as discussed earlier) and a high interfacial viscosity (as shown by Desmaison et al., 1984).

The large oil-water area reflects light well and gives the oil a light brown colour because the light is reflected rather than being absorbed.

Assuming the upper limit of the asphaltene particle molecular weight of 10^4 to 10^5, the size of the asphaltene particle is approximately 4 nm thus the water drop of diameter 3 μm (volume 14×10^{-18} m^3 and area 28×10^{-12} m^2) is surrounded by a volume of asphaltene particles of 0.11×10^{-18} m^3. Now since the water to oil volume ratio in a stable emulsion is typically 5:1 it follows that the oil volume associated with the water is approximately 3×10^{-18} m^3. Thus not more than (0.11/3) or 3.7% of the oil need be asphaltene to provide enough coverage for the water drop. This agrees with the order of magnitude of the measured asphaltene content necessary to stabilize emulsions.

The important conclusion is that even a few percent of asphaltenes is enough to cover water droplets with an effective mechanical barrier to coalescence and reduce electrical conductivity. As Desmaison et al. (1984)

have shown, the interfacial viscosity also increases. Canevari (1987) has even separated a "skin" of this material.

If there is an appreciable resin content the asphaltenic barrier is less rigid and structured and is more easily deformed. The units may be smaller and less ordered. A high aromatic/alkane ratio tends to result in a shift in particle size distribution towards smaller particles which are more "soluble" in the oil medium. Alkane character encourages "precipitation" of asphaltenes around the barrier and thus favours stability.

Wax crystals also may accumulate at the water surface but their naturally hydrophobic character should prevent intimate contact with the water phase unless that phase is shielded by the presence of surface active polar material. This polar material may be present naturally or it may be formed photolytically but its formation can be inhibited by antioxidants. On prolonged exposure to solar radiation the concentration of these polar species increases as does the amount which accumulates at the interface. When a sufficient coverage is obtained it becomes possible for waxes to accumulate at the two dimensional area and form a skin which resists deformation and coalescence.

This is illustrated in Figure 4.1.

It is possible that an oil may have both asphaltene and wax particle accumulation at the interface.

The effect of temperature rise is to increase molecular and particle activity, "dissolve" the asphaltenes and waxes and de-stabilize the emulsion. De-emulsifiers interfere with the processes of particle-particle association in the case of asphaltenes by blocking hydrophylic sites and displacing

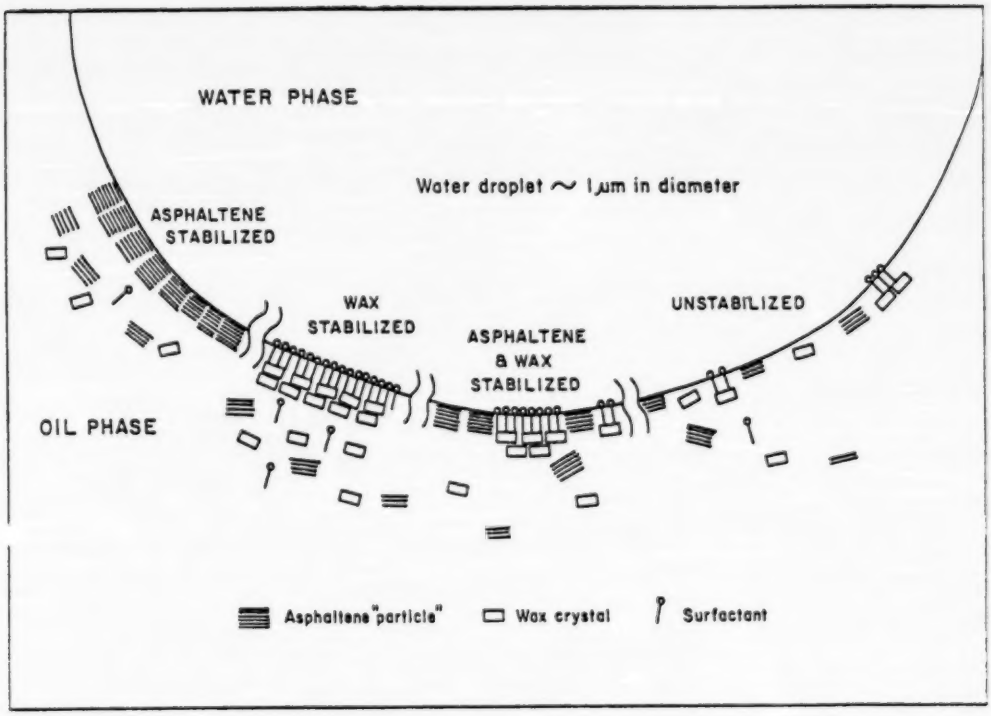

Figure 4.1 Schematic diagram showing a water emulsion droplet in oil (i) stabilized by asphaltenes, (ii) stabilized by surfactants and waxes, (iii) stabilized by both and (iv) unstabilized, i.e. there being incomplete barrier formation.

surfactants from the water interface which can stabilize the location of wax particles.

This mechanism possibly explains the results obtained by Thingstad and Pengerud (1983) who observed that photolysis formed surfactants which gave a (presumably) wax-stabilized emulsion. The antioxidant β-carotene or maintenance in the dark had the same effect of slowing emulsion formation. We hypothesise that different results would have been obtained if the oil had been asphaltene-stabilized.

Oil weathering usually increases emulsion formation and stability. This is believed to be due to a combination of factors, (i) photolysis to form surface active materials, (ii) increases in the concentration of the sparingly soluble asphaltenes and waxes as the more volatile material is lost and (iii) loss of the volatile and soluble aromatics which are good solvents for asphaltenes. The time necessary for phase (i.e. oil-water) separation increases even for nonstabilized systems because of the viscosity increase causing a decrease in Stokes' Law velocity.

Bridie et al. (1980) studied a Kuwait oil with 6.6% asphaltenes and 9.8% waxes which formed a stable emulsion. Removal of both or either wax or asphaltenes resulted in a loss of stability. The removal of 90% of the asphaltenes but with retention of the wax also gave a stable emulsion thus it appears that the asphaltenes are more effective stabilizers, i.e. a lower concentration is required. Asphaltenes appear to be 2.5 to 5 times more effective than waxes as stabilizing agents. Mackay and Zagorski (1982) postulated that the presence of waxes caused increased precipitation of asphaltenes but this is probably erroneous. There may be no interaction between waxes and asphaltenes, they are merely additive in contributing to

formation of a layer which covers the water particles. In the Bridie work it appears that neither the asphaltenes or the waxes alone were capable of covering the available water surface, but in combination complete coverage was possible.

Water particle size plays an important role. The most stable emulsions tend to have particles in the 1 to 5 μm range which, because of their large area/volume ratio require substantial amounts of stabilizing material, i.e. several percent of the oil. Larger water particles (i.e. 10 μm) require less stabilizing material but they have a larger Stokes' Law velocity and tend to coalesce more readily because the barrier is too fragile because its thickness is probably 1/100th to 1/1000th of the drop diameter. The most stable emulsions occur with small, low Stokes' Law velocity drops in which the barrier is a significant fraction (e.g. 1/100th) of the diameter. But this, of course, requires a sufficient supply of barrier material.

Photolysis plays an important role in reducing the oil-water interfacial tension and thus enhancing the rate of formation of emulsions. It is also possible that these surfactants help to stabilize the barrier. Photolysis also may be an important oil breakdown mechanism (Payne and Phillips, 1985a).

Certain strongly surface active chemicals with a high affinity for oil tend to accumulate at the oil-water interface and interfere with the formation of the surface barrier. They therefore de-stabilize emulsions and act to some extent like dispersants. Conventional dispersants are designed to form oil in water emulsions thus they have a high hydrophilic-lipophilic balance (HLB). They thus tend to be fairly soluble in water and may be dissolved rapidly from the oil. The best emulsion inhibitors have a very low water solubility. They

may not be very effective dispersants in the short term, but they may increase dispersion in the long term by delaying water-in-oil emulsion formation.

5. CONCLUSIONS AND RECOMMENDATIONS

In this report we have compiled and reviewed much of the current literature or water-in-oil emulsion formation. Some experimental work has been described. From an examination of this literature a mechanism has been proposed for the formation and stabilization of water-in-oil emulsions.

It is believed that more effort should be devoted to examining and exploiting the considerable surfactant literature as reviewed recently for example by Eicke and Parfitt (1987). This experience has been barely exploited by oil spill scientists.

Further laboratory studies are needed to elucidate the role of photolysis, water chemistry, oil chemistry and turbulence on emulsion formation. If a clearer picture of the processes can be obtained it should be possible to develop better mathematical models and characterize oils according to their emulsification characteristics.

Field studies of the nature of the oil during the onset of emulsification would be invaluable.

Carefully designed and conducted experiments on real and synthetic oils under a variety of conditions should result in a deeper understanding of formation and stability, and thus in a better capability of preventing, or at least forecasting emulsion formation.

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